AKADÉMIAI KIADÓ

Acta Chromatographica

34 (2022) 1, 53–60

DOI:

10.1556/1326.2020.00866

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ORIGINAL RESEARCH PAPER

Application of deep eutectic solvents combined with vortex assisted dispersive liquid-liquid microextraction for five organophosphorus pesticides in juice and green tea beverage

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Received: October 12, 2020 • Accepted: November 13, 2020

Published online: January 19, 2021

ABSTRACT

In this study, a new microextraction method based on hydrophobic deep eutectic solvents was developed for the extraction and preconcentration of organophosphorus pesticides from beverage samples. The hydrophobic deep eutectic solvents were synthesized from choline chloride and 4-chlorophenol. Main experimental parameters of the microextraction method were investigated to improve the extraction efficiency. The proposed method achieved a satisfactory linear range between 50 and 2,000 $\mu\text{g L}^{-1}$ with coefficient of determination greater than 0.9939. The extraction recoveries and enrichment factor of five organophosphorus pesticides at three added levels ranged from 71.68 to 113.18% and 71.43–111.11 were obtained with the acceptable relative standard deviation ranged from 1.37 to 11.92%. Limits of detection and quantification were found to be 0.05–0.3 $\mu\text{g L}^{-1}$ and 0.17–1 $\mu\text{g L}^{-1}$, respectively. Finally, the methods were successfully applied for the determination of five organophosphorus pesticide in orange juice and green tea.

KEYWORDS

beverage, deep eutectic solvents, dispersive liquid-liquid microextraction, organophosphorus pesticides

INTRODUCTION

Organophosphorus pesticides (OPPs) are widely used to control crop pests due to their relatively lower price and highly biological activity. However, the use of pesticides led to the problem of residue in food, and the highly toxic of OPPs to mammals poses a potential health risk to humans. National governments and international organizations around the world have established strict maximum residue limits (MRLs) standards for pesticide residue in food. Thus, the determination of pesticide residue is essential for checking whether the residue in food exceed the MRLs [1, 2]. The composition of matrix are complex and the concentration of pesticides in samples is usually at trace level, detect and quantify pesticides accurately is a difficult task. It is necessary to develop simple, sensitive methods for pesticide residue analysis.

Sample preparation is a critical step for the residue analysis process. Extraction, clean-up, and preconcentration of analytes from samples can be reached by a suitable preparation method [3]. Up to now, classical preparation method include solid phase extraction (SPE) [4, 5], liquid-liquid extraction (LLE) [6], supercritical fluid extraction (SFE) [7] and accelerated solvent extraction (ASE) [8], etc. There are a lot of disadvantages and limits in these methods.

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Large volumes of organic solvents are used in LLE, and only a few microliters are required for instrumental analysis in the end. The disadvantage of solid phase extraction is that the operation is time-consuming and labor-intensive, and the column is disposable, which increases the cost of use. Additional apparatuses were required to provide the extraction conditions for SFE and ASE. The latest research focuses on the development of environmentally friendly sample preparation methods such as microextraction techniques. In particular, the liquid-phase microextraction (LPME) has the advantages of simple, rapid and efficient with a high enrichment factor simultaneously. LPME requires only a few microliters of organic solvents as the extraction solvent. Currently, LPME has many different operating methods, including gas phase and liquid phase methods, like single-drop microextraction (SDME), hollow fiber liquid-phase microextraction (HF-LPME), and dispersive liquid-liquid microextraction (DLLME) [9]. DLLME, developed by Assadi and co-workers in 2006, has become a powerful microextraction technique for the extraction and preconcentration of pesticide residues from various matrices [10]. In DLLME, the extraction solvent was dispersed in the aqueous sample homogeneously, and the extraction process was completed quickly and then separated two phase by centrifugation [11]. After that, the extraction solvent was collected and analyzed to calculate the concentration of analyte by some quantitative method [12–14]. Thus, choosing the desirable extraction solvent is a crucial step for the DLLME. During the early DLLME method, some traditional organic solvents like methylbenzene or chlorobenzene were used as extraction solvent. However, those organic solvents are highly toxic, hard to degrade and easily cause secondary pollution in the environment. Recent studies focused on the DLLME based on green solvent such as ionic liquids (ILs) and deep eutectic solvents (DESs) [15–18]. They were used in liquid-phase microextraction as the extraction solvent and the characteristics of high viscosity and thermal stability were praised by the chemists. The properties of ILs and DESs can be designed by changing the composition of materials. Besides, they have almost no vapor pressure so there are less harmful to operators and environment. But according to the published literatures, some of the materials for the synthesis of ILs are expensive and the preparation conditions are demanding and complex. In contrast, DESs have the low cost, simpler manufacture procedure and better biocompatibility [19]. DESs have been widely applied in electrochemistry [20], organic syntheses [21] and functional material [22], etc. A class of hydrophobic deep eutectic solvents are suitable for dispersive liquid-liquid microextraction as the extraction solvent due to its low solubility in water, high density and viscosity, low volatility, and its ability can be used with liquid chromatography or gas chromatography. In addition, DESs have the characteristics of low toxicity and easy to degrade, meet the requirements of green chemistry. Nowadays, the utilization of DESs in analytical chemistry is still rare, but an increasing number of researchers are focusing on the work of using DESs to detect

trace-level chemicals [23], for the development of microextraction method based on DESs is a promising work.

In this study, a hydrophobic deep eutectic solvents was used as a green extraction solvent for vortex assisted dispersive liquid-liquid microextraction followed by gas chromatography-flame photometric detector (GC-FPD) analysis. A rapid and accurate determination of five organophosphorus pesticides in beverage was successfully established.

MATERIALS AND METHODS

Reagents

Individual standard solutions ($100\text{ }\mu\text{g mL}^{-1}$) prepared in acetone (HPLC grade) of five organophosphorus pesticides (ethoprophos, diazinon, fenitrothion, chlorpyrifos, and profenofos) were obtained from Agro-Environmental Protection Institute Ministry of Agriculture (Tianjin, China). Choline chloride (98%), 4-chlorophenol (99%) and Tetrahydrofuran (THF, 99.9%) were purchased from J&K scientific company (Beijing, China). HPLC grade of acetonitrile were purchased from Sinopharm Chemical Reagent (Shanghai, China). The working standard solutions as required were prepared in acetonitrile by diluting the standard solutions.

Preparation of hydrophobic deep eutectic solvents

Choline chloride (1.3962 g) as hydrogen bond acceptor was mixed with hydrogen bond donor 4-Chlorophenol (3.7968 g) in a screwed cap tube. The tube was transferred into a $75\text{ }^{\circ}\text{C}$ water bath for 15 min and vortexed until forming homogeneous liquid and placed in an ultrasonic bath (500 W) for 5 min to remove bubbles. The hydrophobic deep eutectic solvents (h-DESs) was successfully synthesized after cooling to the room temperature.

Analytical method

Packaged orange juice and green tea were purchased from local supermarket (Beijing, China), Juice and tea beverages were pretreated with centrifugation at 4,000 rpm for 10 min and diluted with an equal volume of deionized water. Five milliliter orange juice or green tea beverages after pretreatment containing five organophosphorus pesticides was transferred into 10 mL centrifuge tube. $100\text{ }\mu\text{L}$ THF as the emulsifier agent and $110\text{ }\mu\text{L}$ h-DESs as the extraction solvent were added into the tube, vortexed for 1 min at room temperature and centrifuged at 3,800 rpm for 5 min. The sedimented phase was diluted with the equal volume of acetonitrile and analyzed by GC system. Typical chromatogram of blank sample (A) and matrix-matched standard solutions of five organophosphorus pesticides (B) were given in Fig. 1.

Instrumentation

The five organophosphorus pesticides were determined on a GC (7890B, Agilent, USA) equipped with a flame photometric detector (FPD) and automatic liquid sampler (7693A, Agilent, USA), The GC was coupled with a split/splitless

Fig. 1. Typical chromatogram of blank sample (A) and matrix-matched standard solutions of five organophosphorus pesticides (B). Five chromatographic peaks labeled by sequential numbers were ethoprophos, diazinon, fenitrothion, chlorpyrifos and profenofos, respectively

injector and was operated in a splitless mode. Chromatographic separation was performed on a DB-1 capillary column (pentadecane 87.7%, 30 m $\times$ 0.250 mm $\times$ 0.25 μ m, Agilent, USA). Nitrogen (99.99%) was used as the carrier gas and make up gas. The carrier gas flow rate was 1 mL min⁻¹ and the makeup gas flow rate was 60 mL min⁻¹. At the beginning, the temperature programming of oven was set at 80 °C, held for 0.5 min. Then elevated to 250 °C at a rate of 25 °C min⁻¹, held for 1 min. At last it was increased to 280 °C at a rate of 35 °C min⁻¹ and maintained for 8 min. Hydrogen gas was produced for FPD at a rate of 75 mL min⁻¹ by a hydrogen generator (KPS-H-500, Beijing, China). High purity compressed air was used at a flow rate at 100 mL min⁻¹. A multi-tube vortexer (UMV-2, China) and a high-speed centrifuge (allegria X-12, Beckman coulter, USA) were used in dispersive liquid-liquid microextraction procedure for mixing and phase separation.

Analytical parameters

Extraction recovery (ER) and enrichment factor (EF) were used to evaluate the DLLME performance in the extraction procedure.

$$ER = \frac{C_{sed} \times V_{sed}}{C_0 \times V_0} \times 100\% \quad (1)$$

$$EF = \frac{V_{sed}}{V_0} \times 100\% \quad (2)$$

where C_{sed} , V_{sed} , C_0 , and V_0 are the concentration and volume of sedimented phase and original sample, respectively.

RESULTS AND DISCUSSION

Optimization of h-DESS

DESSs have a higher density than water and immiscibility in aqueous solution. Composition ratios of h-DESSs affect its properties such as extraction efficiency for target pollutants. Different molar ratios of choline chloride and 4-chlorophenol were (i.e., 1:2, 1:3, 1:4, and 1:5) were selected for the DESSs synthesis in the present study. Effects of composition ratios of h-DESSs on extraction recovery and enrichment factor of five organophosphorus pesticides were investigated. As shown in Fig. 2, extraction recovery of five

Fig. 2. Effect of h-DESS molar ratio on the extraction recoveries of five organophosphorus pesticides. Other extraction condition: 5 mL aqueous solution spiked at $5 \mu\text{g L}^{-1}$ of each pesticide, 110 μL h-DESS as the extraction solvent, 100 μL THF as the emulsifier agent, 5 min as the extraction time

organophosphorus pesticides reach to 69–80% with the molar ratio of 1:4. It may be that the polarity of h-DESS at this ratio is most similar to the analytes.

h-DESS volume played an important role in micro-extraction procedure for five organophosphorus pesticides in juice and green tea drinks. Increased h-DESS volumes (80, 110, 140, and 170 μL) was tested. According to Fig. 3. One hundred and ten microlitre of h-DESS was selected to be the best volume of extractant, because the recoveries increased by the volume from 80 to 110 μL and achieved a good extraction recovery when h-DESS volume was 110 μL . Then little significant increase in the recoveries were observed at higher volume, and some pesticides recovery have even declined. Meanwhile, with the increase of h-DESS volume, the enrichment factor has decreased drastically. For this reason, the optimum volume was chosen as 110 μL .

Optimization of DLLME step

Effect of emulsifier agent. In order to achieved a homogeneous DESSs-aqueous system, tetrahydrofuran (THF) as the

emulsifier agent was added to the original sample [24]. THF was a kind of an aprotic solvent to diminished the tendency of water molecules to interact with h-DESSs molecules. Based on this fact, up to a certain extent, the volume of sedimented phase was depended on the amount of THF. Therefore, a series of samples containing different volume of THF (80, 100, 120, and 140 μL) was investigated. The results shows that the suitable volume of emulsifier agent was 100 μL in Fig. 4. The extraction recovery was increased until the volume of THF reached 100 μL and achieved a satisfied recoveries from 93 to 119%. Afterward, no improvement of performance was observed but decline of enrichment factor with the rise of THF volume. In order to obtain better enrichment factor and minimize the usage of organic solvent, 100 μL was selected as the optimum volume of THF.

Effect of extraction time. There is a certain distribution coefficient between different substances. It is a certain time for pesticide to transfer from sample to h-DESSs but vortex can accelerate mass transfer and significantly reduce the equilibrium time required. Find out the optimized extraction

Fig. 3. Effect of h-DESS volume on the extraction recoveries of five organophosphorus pesticides. Other extraction condition: 5 mL aqueous solution spiked at $5 \mu\text{g L}^{-1}$ of each pesticide, the molar ratio of h-DESS 1:4, 100 μL THF as the emulsifier agent, 5 min as the extraction time

Fig. 4. Effect of THF volume on the extraction recovery recoveries of five organophosphorus pesticides pesticide. Other extraction condition: 5 mL aqueous solution spiked at $5 \mu\text{g L}^{-1}$ of each pesticides, the molar ratio of h-DESS was 1:4, 110 μL h-DESS as the extraction solvent, 5 min as the extraction time

time with high recovery and efficiency is necessary. Thus, the effect of vortex time was tested from 30 s to 5 min (30 s, 1 min, 2 min, and 5 min). Increased extraction recovery was observed in 1 min and then remained nearly constant as shown in Fig. 5. To be specific, all of the improvement of recoveries was no more than 3% when the vortex time increased from 1 to 5 min. Hence, 1 min was chosen to be the vortex time for further study.

Effect of salt addition. Salt addition was widely used in common extraction method. It can be used to decreasing the solubility of pesticide in the aqueous solution by increasing ionic strength, and raising the density of aqueous solution to increase the volume of the organic phase. But in micro-extraction method, less sedimented was expected to achieve a satisfactory enrichment factor. For this purpose, the salt addition effect on this method was investigated by varying concentration of sodium chloride from 0 to 15% (0, 5%, 10%, and 15%, w/v, respectively). The results are shown in Fig. 6. It indicated that this method achieved a great extraction recovery without salt addition. In addition, because of the increased h-DESS volume, enrichment factor

was reduced sharply. So, salt addition was an absent variable in this study.

Study of matrix effect. In order to evaluate the matrix effect, recovery test was applied to contrast the real samples with deionized water. Samples were spiked at 6 concentration levels (50, 100, 250, 500, 1,000, and 2,000 $\mu\text{g L}^{-1}$) of each pesticide and deionized water was spiked at the same concentrations to build regression equation. These ratios of the slope of these standard curves were listed in Table 1.

It is noticed that the matrix effect of samples was too distinct to ignore. In order to eliminate the effects of matrix, all standard solutions for standard curve were diluted with the matrix-matched h-DESS.

Method performance

At this point, appropriate vortex assisted dispersive liquid-liquid microextraction methods have been determined. In order to examine the methodology, it was performed under the optimum conditions to extract five pesticides from orange juice and green tea samples. All sample were spiked at 3

Fig. 5. Effect of vortex time on the extraction recoveries of five organophosphorus pesticides. Other extraction condition: 5 mL aqueous solution spiked at $5 \mu\text{g L}^{-1}$ of each pesticide, the molar ratio of h-DESS 1:4, 110 μL h-DESS as the extraction solvent, 100 μL THF as the emulsifier agent

Fig. 6. Effect of salt addition on the extraction recoveries of five organophosphorus pesticides. Other extraction condition: 5 mL aqueous solution spiked at $5 \mu\text{g L}^{-1}$ of each pesticide, the molar ratio of h-DESs 1:4, 110 μL DESs as the extraction solvent, 100 μL THF as the emulsifier agent, 1 min as the extraction time

Table 1. Slope ratios of matrix and pure solvent regression equation

Pesticide	orange juice	green tea
Ethoprophos	1.958 ^a	1.803
Diazinon	1.256	1.293
Fenitrothion	1.039	0.922
Chlorpyrifos	1.544	1.310
Profenofos	1.511	0.674

^aSlope ratio is calculate from the slope of the regression equation of matrix divided by the slope of the regression equation of pure solvent.

added levels ($1 \mu\text{g L}^{-1}$, $5 \mu\text{g L}^{-1}$, and $50 \mu\text{g L}^{-1}$) with 3 replicates. Table 2 showed that the extraction recoveries ranged from 71.68 to 113.18%, and relative standard deviation ranged from 1.37 to 11.92%.

Furthermore, the limits of detection ($S/N = 3$), limits of quantification ($S/N = 10$), linear range and coefficient of determination (R^2) were investigated and summarized in Table 3.

Comparison with other methods. Comparison of the presented method with other reported methods including solid phase extraction, QuEChERS, liquid-liquid extraction and combination methods for the determination of pesticides in

the various aqueous sample, we confirmed the advantages of the current method. Specifically, due to the high extraction efficiency and enrichment factor of presented method, we successful achieved the lowest limits detection and quantitation even compared to the best performer among these other above-mentioned methods, improved the limits of detection (LODs) and limits of quantitation (LOQs) to 0.05–0.3 $\mu\text{g/L}$ and 0.17–1.0 $\mu\text{g/L}$, respectively, and obtained the extraction recovery which meets the analytical requirements simultaneously. The results are depicted in Table 4 and show that the present method is efficient and sensitive.

CONCLUSIONS

In this study, a rapid, simple and efficient method of vortex assisted with dispersive liquid–liquid microextraction from beverages by GC-FPD was developed. To our best knowledge, it is the first time to use deep eutectic solvents as an extraction solvent in the dispersive liquid–liquid microextraction method for organophosphorus pesticides from beverage. Hydrophobic deep eutectic solvents as an environment-friendly microextraction solvents was introduced in this method. And, above all, the application of the present method achieves a low LOD ($0.05\text{--}0.3 \mu\text{g L}^{-1}$) and LOQ

Table 2. ERs and RSDs of pesticides in samples

Pesticide	1 $\mu\text{g/L}^a$				5 $\mu\text{g/L}$				50 $\mu\text{g/L}$			
	Orange juice		Green tea		Orange juice		Green tea		Orange juice		Green tea	
	ER ^b %	RSD ^c %	ER %	RSD %	ER %	RSD %	ER %	RSD %	ER %	RSD %	ER %	RSD %
Ethoprophos	103.1	2.3	113.2	2.1	87.6	2.1	88.5	2.6	81.3	8.4	83.0	2.0
Diazinon	78.8	3.7	90.8	3.9	86.6	6.5	87.8	7.5	77.8	11.9	82.3	11.1
Fenitrothion	97.2	2.2	71.7	2.1	91.1	8.0	79.8	3.8	77.3	6.8	84.2	2.2
Chlorpyrifos	77.0	4.7	73.4	1.4	83.2	6.4	75.3	2.2	80.8	6.2	77.6	5.6
Profenofos	93.0	3.5	87.3	9.3	87.0	6.8	91.0	5.8	80.2	7.3	93.6	6.8

^aSamples is spiked with each pesticide at three concentrations.

^bExtraction recovery.

^cRelative standard deviation.

Table 3. Analytical linear, LOD and LOQ of the method under the optimum conditions

Pesticide	Sample	Regression equation	R^2 ^b	LOD ^c (µg/L)	LOQ ^d (µg/L)
Ethoprophos	Orange juice	$Y = 6.5451X - 242.51^a$	0.998	0.07	0.22
	Green tea	$Y = 6.0279X - 358.64$	0.994	0.05	0.17
Diazinon	Orange juice	$Y = 1.9439X - 24.063$	0.997	0.18	0.59
	Green tea	$Y = 2.0011X - 68.401$	0.999	0.12	0.38
Fenitrothion	Orange juice	$Y = 2.1535X - 64.248$	0.998	0.2	0.66
	Green tea	$Y = 1.9116X - 48.203$	0.996	0.16	0.54
Chlorpyrifos	Orange juice	$Y = 3.7989X - 63.933$	0.998	0.1	0.34
	Green tea	$Y = 3.2228X - 87.627$	0.999	0.1	0.34
Profenofos	Orange juice	$Y = 1.7481X - 43.455$	0.998	0.22	0.74
	Green tea	$Y = 0.7796X - 27.934$	0.999	0.3	1

^aX and Y are the peak area and concentration (µg/L), respectively.^bCoefficient of determination.^cLimit of detection ($S/N = 3$).^dLimit of quantification ($S/N = 10$).

Table 4. Comparison of the presented method with others

Methods	Pesticides	Matrix	Recovery (%)	LOD ^a (µg/L)	LOQ ^b (µg/L)	Reference
3D-GA-SPE-GC/MS ^c	Trichlorfon, ethoprophos, dimethoate, fenitrothion, parathion, fenthion	Water	93.8–104.2	0.12–0.58	0.41–1.96	[25]
QuEChERS-UHPLC/MS-MS ^d	Diazinon, ametryn, penconazole, diniconazole, fenazaquin	Honey	70–120	5	10–25	[26]
d-SPE-DLLME-GC-FID ^e	Diazinon, ametryn, chlorpyrifos, penconazole, oxadiazon, diniconazole fenazaquin	Fruit juices	49–75	0.15–0.36	0.49–1.2	[27]
LLE-DLLME-GC-FID ^f	Fenazaquin, oxadiazon, diniconazole, penconazole, ametryn, chlorpyrifos, diazinon	Honey	56–86	0.32–1.2	1.1–4.0	[28]
DLLME-GC-FPD ^g	Ethoprophos, diazinon, fenitrothion, chlorpyrifos profenofos	juice, tea	72–113	0.05–0.3	0.17–1.0	present method

^aLimit of detection ($S/N = 3$).^bLimit of quantification ($S/N = 10$).^cThree dimensional graphene airgel-solid phase extraction-gas chromatography/mass spectrometry.^dQuick, easy, cheap, effective, rugged, safe-ultra high performance liquid chromatography/mass spectrometry-mass spectrometry.^eDispersive-solid phase extraction-dispersive liquid liquid microextraction-gas chromatography-flame ionization detector.^fLiquid liquid extraction-dispersive liquid liquid microextraction-gas chromatography-flame ionization detector.^gDispersive liquid liquid microextraction-gas chromatography-flame photometric detector.

(0.17–1 µg L⁻¹), widely linear range (50–2,000 µg L⁻¹), good linear relationship ($R^2 > 0.9939$), satisfactory enrichment factor (71.43–111.11) and extraction recovery (71.68–113.18%) with an accepted relative standard deviation (1.37–11.92%). Overall, this method can be applied for determination of these five organophosphorus pesticide in beverage samples. Our work further confirmed that the hydrophobic deep eutectic solvents have the ability to achieve extraction, purification and preconcentration of organophosphorus pesticides from aqueous matrices efficiently.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Science and Technology of China (National Key Research and

Development Plan, 2016YFD0200208), Beijing Academy of Agricultural and Forestry Sciences, (Overseas Program, Platform Project KJCX20200302-06), and National Natural Science Foundation of China (31301694).

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